

# Dependence of RIP(K) and RIP(N) of natural and urban sorbents on K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> concentration

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**Abstract.** The technique of Waters et al. [4] was modified using a range of K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> concentrations (from 0.1 to 16 mM dm<sup>-3</sup>) instead of the fixed K<sup>+</sup> concentration (0.5 mM dm<sup>-3</sup>). The plot of K<sub>d</sub><sup>-1</sup> of <sup>137</sup>Cs vs K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> concentration gives a single line or two lines depending on the material studied. The Langmuir-like competitive sorption isotherm equation was proposed to describe the product of <sup>137</sup>Cs distribution coefficient K<sub>d</sub> on the competitive monovalent cation M<sup>+</sup> concentration C<sub>M</sub>. Main parameters of the equation are the maximal radiocesium interception potential RIP(M)<sub>max</sub> and the affinity constant B(M). The K<sub>d</sub>C<sub>M</sub> value is designated as RIP(M). The Langmuir-like equation satisfactorily describes the dependence of RIP(M) on C<sub>M</sub>. When two types of adsorption sites participate in the <sup>137</sup>Cs selective sorption process simultaneously the <sup>137</sup>Cs selective sorption can be described by RIP(M)<sub>max</sub> and the affinity constant for high and low affinity sites, respectively. The high affinity sites are associated with the increased capacity of specific sorption sites at low C<sub>M</sub>. This was indirectly confirmed by the effect of the reducing the <sup>137</sup>Cs exchangeable fraction with a decrease in C<sub>M</sub>.

## 1. INTRODUCTION

Selective sorption of <sup>137</sup>Cs is the main mechanism affecting its behavior in mineral sorbents including nonorganic soils. It is generally accepted that when the regular exchange sites are masked by the excess, for example of Ca<sup>2+</sup>, <sup>137</sup>Cs specific sorption takes place at the frayed edge sites (FES) of the illite type clay minerals. The main cations M<sup>+</sup>, which compete with <sup>137</sup>Cs, are K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>. Such bivalent cations as Ca<sup>2+</sup> and Mg<sup>2+</sup> are believed to have no access to the FES due to the steric reasons [1]. The postulates used in the deriving the equations relating the distribution coefficient of <sup>137</sup>Cs K<sub>d</sub> with M<sup>+</sup> are the independence of the FES capacity on M<sup>+</sup> concentration and application of the regular ion exchange laws to the <sup>137</sup>Cs and M<sup>+</sup> reactions on FES [2, 3]. The following equation is widely used to describe the dependence of the K<sub>d</sub> <sup>137</sup>Cs on C<sub>M</sub>:

$$K_d = \frac{K_c^{FES}(Cs/M) \cdot [FES]}{C_M} \cdot Z_M^{FES}, \quad (1)$$

where  $K_c^{FES}(Cs/M)$  is the selectivity coefficient between trace quantities of Cs<sup>+</sup> and M<sup>+</sup> on FES, [FES] is the FES capacity,  $Z_M^{FES}$  is the fractional loading of

$M^+$  on FES. If we denote the product of  $K_C^{FES}(Cs/M)$  on [FES] as a radiocesium interception potential in relation to the competitive cation  $M^+$  RIP(M), and assume that the value of  $Z_M^{FES}$  equals 1 (providing the  $C_{Cs} \ll C_M$ , which is true for the environmental levels of  $^{137}Cs$ ), we obtain a simple and widely used equation:

$$K_d = \frac{RIP(M)}{C_M} \quad (2)$$

That is,  $K_d$  of  $^{137}Cs$  directly proportional to the RIP(M) and inversely proportional to the concentration of a competitive cation  $M^+$ . The RIP(M) is usually determined by the plateau value of the plot of the  $K_d C_M$  vs  $C_M$ , or by the determination of the FES capacity and  $K_C^{FES}(Cs/M)$  value, or by equating the  $K_d C_M$  product to the RIP(M) at specified conditions as in the simplified method of RIP(M) determination proposed by Waters et al. [4]. The RIP(M) value is a valuable parameter as it gives the straightforward way of determining the  $K_d$  value. However, the equation (2) is derived for  $M^+$  concentrations from about one to several mM  $dm^{-3}$ . Moreover, if the plateau can be more or less easily determined for such a clay mineral as illite, the plateau value for clinoptilolite which has no specific sorption sites like FES but has marked selectivity due to the developed microporosity is difficult to determine.

An alternative approach can be proposed to determine the  $^{137}Cs$  selective sorption. It consists in using the linearization procedure of  $K_d$  dependence on  $C_M$  in a narrow  $C_M$  range to fit Langmuir-like equation and on this basis predicting  $^{137}Cs$  sorption in the more wide  $C_M$  range.

The approach of Wuster et al. [5] can be used to describe the competitive sorption of  $Cs^+$  and  $M^+$  by the Langmuir-like equation but assuming that the maximal selective sorption of cesium  $X_{max}$  equals that of  $M^+$ :

$$X_{Cs} = \frac{B(Cs) \cdot C_{Cs}}{1 + B(M) \cdot C_M + B(Cs) \cdot C_{Cs}} \cdot X_{max}, \quad (3)$$

where  $X_{Cs}$  is the amount of sorbed  $Cs^+$ ,  $C_{Cs}$  is the  $Cs^+$  concentration,  $B(M)$  and  $B(Cs)$  are the affinity constants of  $M^+$  and  $Cs^+$ , respectively. Dividing both sides of the equation (3) on  $C_{Cs}$  and transforming, we obtain:

$$\frac{1}{K_d} = \frac{1 + B(M) \cdot C_M + B(Cs) \cdot C_{Cs}}{X_{max} \cdot B(Cs)} \quad (4)$$

For  $^{137}Cs$ , we can assume that  $C_{Cs} \rightarrow 0$  and  $B_{Cs} \cdot C_{Cs} \rightarrow 0$ , therefore:

$$\frac{1}{K_d} = \frac{1}{X_{max} \cdot B(Cs)} + \frac{1}{X_{max} \cdot \frac{B(Cs)}{B(M)}} \cdot C_M \quad (5)$$

Denoting  $X_{max} \cdot \frac{B(Cs)}{B(M)} = RIP(M)_{max}$ , where  $RIP(M)_{max}$  is the maximal radiocesium interception potential, mM  $kg^{-1}$ , we obtain the linear form of the Langmuir-like equation:

$$\frac{1}{K_d} = \frac{1}{RIP(M)_{max} \cdot B(M)} + \frac{1}{RIP(M)_{max}} \cdot C_M \quad (6)$$

From this equation it follows that the dependence of  $K_d^{-1}$  from  $C_M$  is described by a straight line. The angle of the slope is equal to  $1/RIP(M)_{max}$ , and

the intercept on the ordinate axis is equal to  $1/(RIP(M)_{\max}B(M))$ . Denoting  $K_d C_M$  as  $RIP(M)$  we obtain:

$$K_d \cdot C_M = RIP(M) = \frac{B(M) \cdot C_M}{1 + B(M) \cdot C_M} \cdot RIP(M)_{\max} \quad (7)$$

That is, when  $C_M \rightarrow \infty$

$$K_d = \frac{RIP(M)_{\max}}{C_M} \quad (8)$$

Equation (8) is equivalent to the equation (2). When  $C_M \rightarrow 0$

$$K_d = B(M) \cdot RIP(M)_{\max} \quad (9)$$

The derived equations are valid for the scenario when FES capacity is a constant and does not depend on  $C_M$ . Let us consider the second possible scenario when FES capacity is not a constant but varies as a result of the potassium depletion from the interlayers of clay minerals at low  $C_M$ . There are no straightforward proof of the phenomenon at the environmental concentrations of cations but Sawhney [6] and Tamura [7] showed that the removal of  $K^+$  from the interlayer spaces of biotite and illite with a tetraphenylborate solution increased the sorption of  $Cs^+$ . The indirect evidence of the interlayers expansion and increasing the  $^{137}Cs$  access to the specific sorption sites is the exchangeable fraction of  $^{137}Cs$  ( $\alpha_{Ex}$ ). Smith and Comans [8] showed the increase of  $\alpha_{Ex}$  in bottom sediments of the freshwater lake with increasing  $NH_4^+$  concentration ( $C_N$ ). De Koning and Comans [9] postulated the existence of the threshold  $C_N$  when illite interlayers are in complete collapse and  $\alpha_{Ex}$  as determined by 1 M ammonium acetate extraction does not change with increasing  $C_N$ . The  $\alpha_{Ex}$  can be an indicator of the amount of  $^{137}Cs$  trapped inside the clay mineral interlayers thus showing indirectly the degree of change of specific sorption sites capacity.

The goal of this study is to check the equations presented above to describe the  $K_d$  dependence of the selectively sorbed  $^{137}Cs$  in natural sorbents and such urban materials as granite and concrete on  $K^+$  and  $NH_4^+$  concentrations at sufficiently high background concentration of  $Ca^{2+}$ . Another goal was to simultaneously determine the dependence of  $\alpha_{Ex}$  in the sorbents studied on  $C_K$  and  $C_N$ .

## 2. MATERIALS AND METHODS

### 2.1 Materials

The following sorbents have been studied: Fithian illite (ILLITE) (Illinois, USA), CH clinoptilolite (CLINOPT) (Teaque Mineral Product, Oregon, USA), tripolite (TRIPL) from Zikeevo deposit and dark-cherry bentonite (BENT) from Fersikovo deposit of Kaluga region, RF; granite (GRAN) and concrete (CONCR) were supplied from IPA USA in the frame of the ISTC project 4007. The sorbents were ground in a porcelain mortar and sieved through a sieve with a mesh diameter of 0.25 mm. Table 1 summarizes some properties of the sorbents studied. References in which properties are described are provided in brackets after the corresponding value.

The actual ( $pH(H_2O)$ ) and exchangeable ( $pH(KCl)$ ) acidity were determined by known procedures [10]. The cation exchange capacity (CEC) was determined by the  $BaCl_2$  method at pH 6.5 [11]. The metal content was determined using the procedure accepted by the Hydrometeorological Service of the RF [12]. The values

of lost on ignition (LOI) was determined at 1000 °C, RIP(K) and RIP(N) was determined according [4].

**Table 1.** Physicochemical properties of the sorbents studied, on absolute dry weight.

	CLINOPT	ILLITE	BENT	TRIPL	GRAN	CONCR
RIP(K), mM kg <sup>-1</sup>	1798±2 5	7740±54	5860±2 40	3136±35	204±22	185±5
RIP(N), mM kg <sup>-1</sup>	2700±1 30	1242±32	1183±2 9	582±10	11.4±0.9	195.4±1. 5
CEC, cM(+)kg <sup>-1</sup>	45.8±1. 6	20.2±.1.2	24.9±1. 8	29.2±2.5	5.9±0.6	-
pH(H <sub>2</sub> O)	7.3	5.4	7.4	3.8	10.0	12.3
pH(KCl)	5.2	4.9	6.8	4.3	9.7	12.5
CaO, %	0.98 [13]	0.51 [14]	0.12	1.2 [15]	17.39	4.12
MgO, %	0.20 [13]	3.31 [14]	1.60	0.3-0.9 [15]	0.54	1.90
BaO, %	-	-	0.02	-	0.16	0.03
K <sub>2</sub> O, %	4.78 [13]	5.78 [14]	0.13	0.6-2.0 [15]	3.21	0.92
Na <sub>2</sub> O, %	1.41 [13]	0.32 [14]	-	-	6.74	0.75
Al <sub>2</sub> O <sub>3</sub> , %	11.4 [13]	22.18 [14]	29.48	4.5 [15]	16.05	7.71
Fe <sub>2</sub> O <sub>3</sub> , %	2.15 [13]	9.08 [14]	5.81	2-3.5 [15]	1.29	3.95
MnO, %	0.02 [13]	-	0.02	-	0.01	0.04
SiO <sub>2</sub> , %	66.5 [13]	46.96 [14]	-	-	-	-
TiO <sub>2</sub> , %	0.32 [13]	-	-	-	-	-
LOI, %	6.24±0. 03	7.31±0.0 3	9.07±0. 01	3.64±0.0 3	0.238±0. 01	11.26±0. 01

## 2.2 Determination of RIP(M) and $\alpha_{\text{Ex}}$ as a function of $C_M$ by the batch method

To determine the RIP(M) values we used the batch method suggested by Wauters et al. [2] modified to study the influence of the concentration of the competing cation  $M^+$ . The sorbents (0.2 g) were placed in polycarbonate centrifuge tubes. Samples were preequilibrated three times with 50 cm<sup>3</sup> of a solution containing 100 mM dm<sup>-3</sup> Ca<sup>2+</sup> and K<sup>+</sup> (0.5-16 mM dm<sup>-3</sup>) or NH<sub>4</sub><sup>+</sup> (0.125-16 mM dm<sup>-3</sup>) during 24 hours. After each equilibration the phases were separated by centrifugation and the liquid phase was discarded. Then 50 cm<sup>3</sup> of a similar solution containing 1 kBq of <sup>137</sup>Cs was added to the centrifuge tube, and the suspension was shaken on to-and-fro shaker for 24 hours (<sup>137</sup>Cs stock solution contained 0.2 µg of CsNO<sub>3</sub> per kBq of <sup>137</sup>Cs). After centrifugation the <sup>137</sup>Cs specific activity in the liquid phase was determined on a Wizard 1480 gamma-counter with NaI(Tl) crystal detector. The RIP(M) values were calculated by the formula:

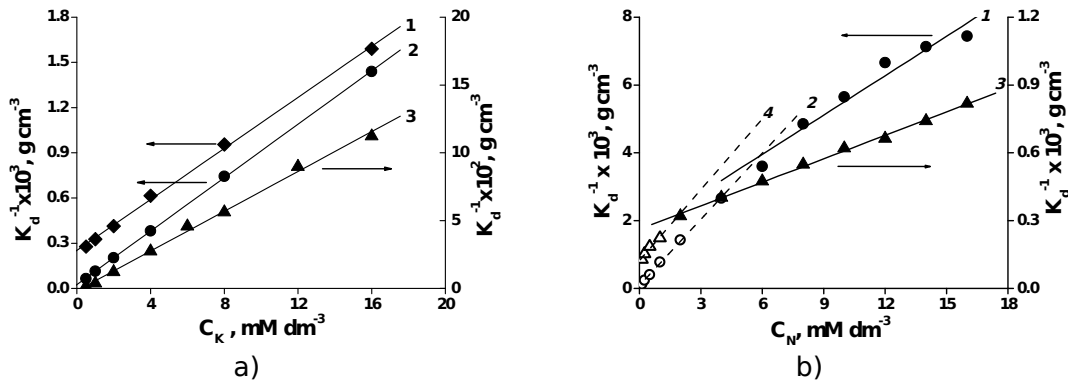
$$\text{RIP}(M) = \frac{V(C_0 - C_e)C_M}{m_s C_e}, \quad (10)$$

where  $C_0$  is the initial specific activity of  $^{137}\text{Cs}$  in solution,  $\text{kBq dm}^{-3}$ ,  $C_e$  is the equilibrium specific activity of  $^{137}\text{Cs}$  in solution,  $\text{kBq dm}^{-3}$ ,  $V$  is the solution volume,  $\text{dm}^3$ ,  $m_s$  is the sorbent mass,  $\text{kg}$ , and  $C_M$  is the  $M^+$  concentration in solution,  $\text{mM dm}^{-3}$ . The experiments were performed at  $22 \pm 2$  °C for natural sorbents, and  $20 \pm 1$  °C for urban materials.

The exchangeable fraction of selectively sorbed  $^{137}\text{Cs}$   $\alpha_{\text{Ex}}$  was determined by extraction of a sorbent left after the determination of  $\text{RIP}(M)$  in the centrifuge tube with a 1 M ammonium acetate solution for 1 hour. The  $\alpha_{\text{Ex}}$  value is the ratio of the  $^{137}\text{Cs}$  activity in the  $50 \text{ cm}^3$  of 1 M ammonium acetate solution and the sorbed  $^{137}\text{Cs}$  activity.

### 3. RESULTS AND DISCUSSION

The results of the dependence of the  $^{137}\text{Cs}$  selective sorption on  $C_M$  are shown in Fig. 1. Its indicate that the linear dependence of  $K_d^{-1}$  in the  $C_K$  range from 0.5 to 16  $\text{mM}$  holds for clinoptilolite, illite and granite (Fig. 1a). The dependence of  $K_d^{-1}$  of  $^{137}\text{Cs}$  on the  $\text{NH}_4^+$  concentration for illite and clinoptilolite (Fig. 1b) as well as bentonite and tripolite is not linear but can be described by two straight lines. One of these lines describes the concentration range from 0 to  $\approx 3 \text{ mM}$  (curves 2 and 4), and the other, the concentration exceeding 3  $\text{mM}$  (curves 1 and 3). This dependence suggests the presence of two types of selective sorption sites: high affinity sites (H) are filled at low  $C_N$ , and low affinity sites (L), at high  $C_N$ . The maximal radiocesium interception potentials  $\text{RIP}(N)_{\text{max}}^{\text{H}}$  and  $\text{RIP}(N)_{\text{max}}^{\text{L}}$  and the corresponding affinity coefficients  $B(N)^{\text{H}}$  and  $B(N)^{\text{L}}$ , respectively, can be attributed to these sorption sites.



**Figure 1.** a) Plot of  $K_d^{-1}$  of  $^{137}\text{Cs}$  vs.  $\text{K}^+$  concentration: (1) clinoptilolite, (2) illite, (3) granite. b) Plot of  $K_d^{-1}$  of  $^{137}\text{Cs}$  vs.  $\text{NH}_4^+$  concentration: (1, 2) illite (3, 4) clinoptilolite; see also comments in the text.

The  $\text{RIP}(M)_{\text{max}}^{\text{H}}$  and  $\text{RIP}(M)_{\text{max}}^{\text{L}}$  and the corresponding affinity coefficients for both competing cations are given in Table 2.

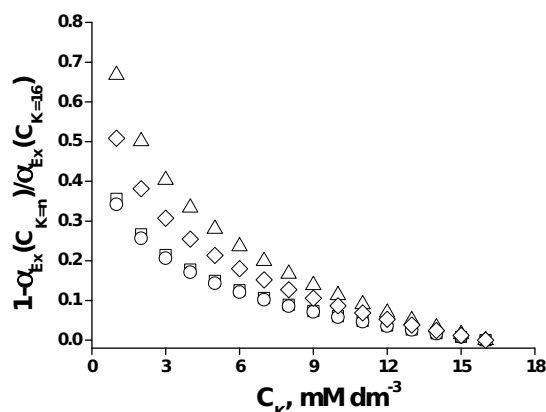
**Table 2.** The values of  $\text{RIP}(M)_{\text{max}} \times 10^{-3} (\text{mM kg}^{-1})$  and  $B(M) (\text{dm}^3 \text{mM}^{-1})$  for natural and urban sorbents, on absolute dry weight.

	CLINOPT	ILLITE	BENT	TRIPL	GRAN	CONCR
$\text{RIP}(K)_{\text{max}}$	$11.81 \pm 0.23$	$11.31 \pm 0.05$	-	-	$136 \pm 3$	-

B	$0.336 \pm 0.023$	$3.4 \pm 0.5$	-	-	$4.0 \pm 3.1$	-
$RIP(K)_{max}^H$	-	-	$8.5 \pm 0.4$	$5.6 \pm 0.1$	-	$224 \pm 10$
$B(K)^H$	-	-	$3.4 \pm 0.9$	$2.43 \pm 0.18$	-	$5.8 \pm 2.3 \pm$
$RIP(K)_{max}^L$	-	-	$13.9 \pm 0.4$	$8.9 \pm 0.4$	-	$539 \pm 50$
$B(K)^L$	-	-	$0.30 \pm 0.04$	$0.36 \pm 0.07$	-	$0.23 \pm 0.07$
$RIP(N)_{max}^H$	$9.6 \pm 1.4$	$1.54 \pm 0.03$	$1.41 \pm 0.07$	$0.69 \pm 0.03$	-	-
$B(N)^H$	$0.84 \pm 0.18$	$7.6 \pm 2.2$	$16.8 \pm 8.3$	$10.9 \pm 2.0$	-	-
$RIP(N)_{max}^L$	$28.9 \pm 0.6$	$2.59 \pm 0.27$	$2.16 \pm 0.13$	$1.54 \pm 0.09$	-	-
$B(N)^L$	$0.13 \pm 0.01$	$0.24 \pm 0.09$	$0.9 \pm 0.5$	$0.53 \pm 0.16$	-	-

For illite, the  $RIP(N)_{max}^H$  and  $RIP(N)_{max}^L$  are considerably lower ( $1.5$  and  $2.5$   $M\ kg^{-1}$ ) than for clinoptilolite ( $9.5$  and  $29.9$   $M\ kg^{-1}$ , respectively). However, these sorbents differ very strongly in the affinity coefficients  $B(N)^H$  and  $B(N)^L$  ( $7.6$  and  $0.24\ dm^3\ mM^{-1}$  for illite,  $0.85$  and  $0.13\ dm^3\ mM^{-1}$  for clinoptilolite). These trends confirm the considerably higher affinity of  $^{137}Cs$  for illite compared to clinoptilolite [3].

According to the Fig 1b illite exhibits the highest affinity for  $^{137}Cs$  at high  $^{137}Cs$  loadings (low  $M^+$  concentrations). The sorption sites with high affinity is expected to be filled first and the total sorbent affinity for  $^{137}Cs$  will decrease with increasing  $^{137}Cs$  sorption. However, high  $^{137}Cs$  affinity at low  $C_M$  suggests a change in the properties of the sorbent. The high  $^{137}Cs$  affinity is supposed to be the result of an increase in the number of selective sorption sites due to the depletion of potassium from the illitic mineral interlayers at low  $C_M$ . The concentration dependence of  $^{137}Cs$  adsorption on  $C_M$  can be assessed indirectly by determining the exchangeable  $^{137}Cs$  fraction  $\square_{Ex}$ . If the amount of  $^{137}Cs$  selective sites increases when  $C_M$  decreases then  $\square_{Ex}$  value will be decreasing. The most convenient way of comparing the dependence of  $\square_{Ex}$  on  $C_M$  for different sorbents is to use the ratio of the  $^{137}Cs$  exchangeable fraction  $\square_{Ex}(C_{M=n})$ , where  $n$  is the numerical value of  $C_M$  ( $mM\ dm^{-3}$ ) to the  $\square_{Ex}$  at  $C_M = 16\ mM\ dm^{-3}$ , when the clay mineral interlayers can be postulated to be in the complete collapse. The dependence of the ratio  $1 - \square_E(C_{K=n})/\square_E(C_{K=16})$  is shown on Fig. 2. It can be seen that the  $1 - \square_E(C_{K=n})/\square_E(C_{K=16})$  for all sorbents increases considerably at low  $C_K$  indicating the possibility of increasing the number of selective sorption sites.



**Figure 2.** Normalized exchangeable fraction of selectively sorbed  $^{137}\text{Cs}$  as a function of the  $\text{K}^+$  concentration:  
 $\triangle$  - granite;  $\bullet$  - concrete;  $\square$  - illite;  $\circ$  - tripolite.

#### 4. CONCLUSIONS

The mechanistic approach is proposed to describe the dependence of  $^{137}\text{Cs}$  selective sorption on  $\text{K}^+$  or  $\text{NH}_4^+$  concentration using the competitive Langmuir-like equation. This equation relates the product of  $C_M K_d$  (or the radiocesium interception potential relative the competing cation  $\text{M}^+$ ,  $\text{RIP}(\text{M})$ ) with the maximal radiocesium interception potential  $\text{RIP}(\text{M})_{\text{max}}$  and affinity constant  $B(\text{M})$ . The product  $C_M K_d$  is denoted as  $\text{RIP}(\text{M})$  because the  $K_d$  value can be calculated at any  $C_M$ .

Two types of the  $K_d^{-1}$  relationships on  $C_M$  have been observed for natural sorbents. The linear dependence of  $K_d^{-1}$  in the  $C_K$  range from 0.5 to 16 mM holds for clinoptilolite, illite and granite. The dependence of  $K_d^{-1}$  of  $^{137}\text{Cs}$  on the  $\text{NH}_4^+$  concentration for illite and clinoptilolite, bentonite and tripolite can be described by two straight lines.

Sorbents exhibit the highest affinity for  $^{137}\text{Cs}$  at high  $^{137}\text{Cs}$  loadings (low  $\text{M}^+$  concentrations). However, high  $^{137}\text{Cs}$  affinity at low  $C_M$  suggests a change in the properties of the sorbent. The high  $^{137}\text{Cs}$  affinity at low  $C_M$  is supposed to be the result of an increase in the number of selective sorption sites due to the depletion of potassium from the illitic mineral interlayers. This possibility is indirectly confirmed by the decrease of the exchangeable  $^{137}\text{Cs}$  fraction  $\alpha_{\text{Ex}}$  with a decrease in  $C_M$ .

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